

Numerical Analysis of Surface Chemical Species and NO_x Reduction Improvement over a Fe-zeolite Catalyst in an NH₃-SCR System on a Diesel Engine

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Abstract: To fulfill the increasingly stringent emission regulations, several technologies have been developed in the past to eliminate pollutants from the exhaust gas of diesel-powered engines. Around this subject matter, a lot of research efforts have been put to find suitable catalytic systems and to understand the mechanistic backgrounds of chemical processes on the catalytic surface. One technology for NO_x reduction in vehicles as well as in other combustion processes is to use Selective Catalytic Reduction which utilizes ammonia as reducing agent (NH₃-SCR). The Fe-zeolite catalyst has been selected in this research study. However, NO_x reduction of SCR system is significantly worse at low catalyst temperature. The experiments have been conducted to validate the numerical model at catalyst temperature 224 °C for further study which cannot be analyzed from the experimental results. This study thus aims at understanding the way enriching NO_x conversion by analyzing SCR catalyst surface chemical species such as O₂⁻, H⁺, NH₄⁺, NH₄NO₃, NO₃⁻ and NO₂⁻ at both during supplying and cutting off NH₃ injection. The numerical analysis shows chemical reactions are much more active at upstream and upper layer than that at downstream and lower layer of the catalyst. In addition, the NO_x conversion is enhanced when the catalyst temperature rises accordingly. This improvement of NO_x reduction is attributed from fast chemical reaction rates when temperature is appropriately high. Remarkably, the NO_x is still in a high conversion rate after immediately cutting NH₃ supply for a quick period before recovering to the initial state due to the occurrence of NH₄NO₃ decomposition. Consequently, it can be concluded that supplying and cutting off NH₃ for a while is efficient and helps improve the total NO_x conversion efficiency.

Keywords: Diesel engine-out NO_x; NH₃-SCR; Surface chemical species; NH₄NO₃ decomposition

1. INTRODUCTION

Firstly, the focuses went to fuel efficiency and durability of the engine operation. Nowadays, a challenge in the development of diesel vehicles for advanced technology supplementary to engine modification is the limitation of exhaust pollutant emissions in order to fulfill the increasingly stringent regulation, especially in relation to

nitrogen oxides NO_x and particulate matter PM. NO_x is a very harmful gas to both human health and environment. It reacts with other substances to cause mainly ground-level ozone (smog) and acid rain so that human health concerns include effects on breathing and respiratory system and lung tissue damage.

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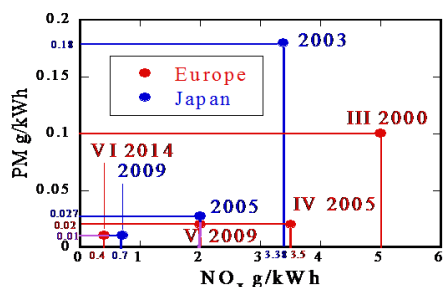
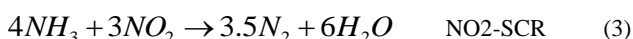
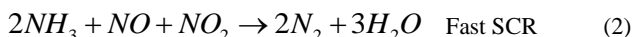
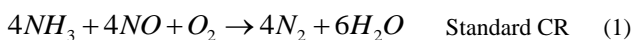


Figure 1. Emission regulation standards of heavy-duty diesel in Europe and Japan.

In addition, the emission legislation has substantially changed its picture which demands for lower emissions. The increasingly more stringent in Euro VI (2014) and JP 09 emission regulations standard have been established for manufacturers to attain shown in figure 1.

SCR technology is known as a most promising technique for heavy-duty diesel engine-out NO_x abatement to help meet these regulations (Koebel, 2000). It utilizes urea or ammonia injected at the upstream of the catalyst as reducing agent to catalytically convert NO_x to harmless nitrogen and water via global chemical reactions (1)-(3). Around this topic a lot of research efforts have been done to understand the mechanism of the chemical reaction progress on the catalyst surface. On top of that, kinetics model have been made and published by many researchers.



The reaction (1) is generally known as “Standard SCR” since the reaction rate is fast and NO_x normally consists of primarily more NO to NO_2 in the diesel exhaust gas. The next reaction is called “Fast SCR” and plays an important role in the NO_x conversion especially at low temperature because its reaction rate can be faster than standard SCR. The reaction (3) is known as “ NO_2 -SCR” reaction. Nonetheless, besides the advantages of SCR catalyst system utilization, it also has its drawbacks in low NO_x conversion efficiency at low temperature range.

2. SCR MODELING

For the calculation, the model has been constructed by choosing one sample channel of SCR catalyst and gridding into 10 cells as shown in figure 2 and involving the mass balance and energy balance (渡邊 Toyota vol.37 No. 3) which have been schematized in figure 3. The exhaust gas flows at gas phase from cell 1 and across to catalyst layers from cell 2. It means there is no reaction on the

catalyst surface on cell 1. The study of chemical reactions will begin from cell 2 to cell 10.

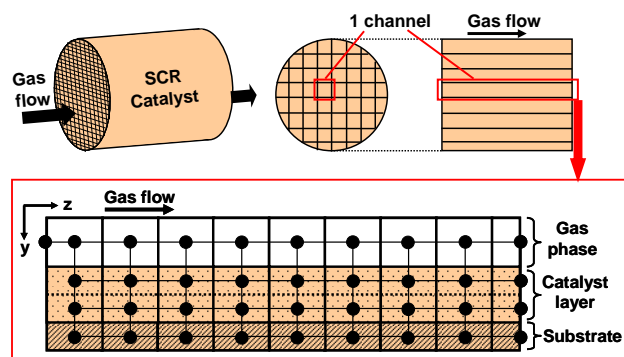


Figure 2. Computational grid of a chosen channel.

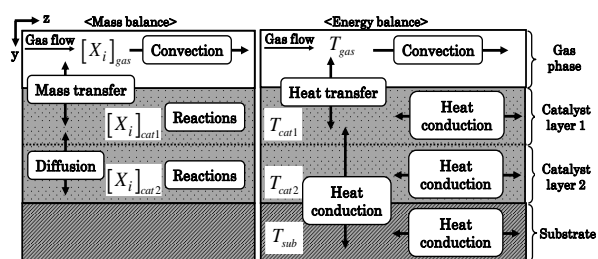


Figure 3. Illustration of mass balance and energy balance.

To make the model simpler while keeping a good accuracy, some assumptions and simplifications have been dedicatedly made such as all channels are geometrically identical, all channels are thermally identical and one channel represents entire other channels of the SCR catalyst honeycomb type.

The reactions (1)-(3) merely represent the global or principle of chemical reactions occurred on SCR catalyst. Eventually, there are many other intermediate chemical reactions are formed and decomposed. All of the reactions involved in the $\text{NO-NO}_2/\text{NH}_3$ chemistry have been expressed conventionally in terms of molecular species and likely related surface adspecies (Grossale, 2008). In addition, the table 1 illustrates the chemical reactions that have been taken into consideration for SCR modeling.

Table 1. Chemical reactions considered in the SCR modeling.

(R1) $H_2O + 2\sigma_w + \gamma \rightleftharpoons 2\sigma_w H^+ + \gamma O^{2-}$	(R7) $2NO + O_2 \rightleftharpoons 2NO_2$
(R2) $\sigma_w H^+ + \sigma_s \rightleftharpoons \sigma_w + \sigma_s H^+$	(R8) $\sigma_w NH_4^+ + \gamma NO_2^- \rightarrow N_2 + 2H_2O + \sigma_w + \gamma$
(R3) $NH_3 + \sigma_w H^+ \rightleftharpoons \sigma_w NH_4^+$	(R9) $\sigma_w NH_4^+ + \gamma NO_3^- \rightleftharpoons \gamma NH_4NO_3 + \sigma_w$
(R4) $\sigma_w NH_4^+ + \sigma_s H^+ \rightleftharpoons \sigma_w H^+ + \sigma_s NH_4^+$	(R10) $\gamma NH_4NO_3 \rightarrow N_2O + 2H_2O + \gamma$
(R5) $2NO_2 + \gamma O^{2-} + \gamma \rightleftharpoons \gamma NO_2^- + \gamma NO_3^-$	(R11) $2\sigma_w NH_4^+ + 2O_2 \rightarrow 2\sigma_w + N_2 + 4H_2O$
(R6) $NO + \gamma NO_2^- \rightleftharpoons NO_2 + \gamma NO_2^-$	(R12) $4NO + O_2 + 4\sigma_w NH_4^+ \rightleftharpoons 4N_2 + 6H_2O + 4\sigma_w H^+$

σ_w : Weak acid site σ_s : Strong acid site γ : Base site

3. RESULTS AND DISCUSSION

3.1 Experimental and numerical results at 224 °C

It is suggested that the composition of exhaust gases are mostly of NO about 90% and small amount of NO₂. It was reported that increasing the NO₂ fraction in the feed can improve NO_x conversion over commercial Fe-zeolite over a diesel engine by Kröcher et al. (2006). Colombo et al. (2011) reported that it was evident that the deNO_x performance of the catalyst is worse for the limiting situations where either the NO or NO₂ are the only specie (NO₂/NO_x=0 or 1) present in the reacting system together with the NH₃. However, better performance were seen with the mixture of NO_x feed containing 25% of either NO or alternatively by far. In addition, equimolar amount of NO and NO₂ was shown the best which is associated with activity of the Fast-SCR reaction (2).

$$NO_x \text{ conversion efficiency} = \frac{NO_{x,inlet} - NO_{x,outlet}}{NO_{x,inlet}} \times 100\% \quad (4)$$

The NH₃ emitted to ambient air is limited to be less than 10 ppm because it can react with sulfuric acid and nitric acid to form ammonium sulfate and ammonium nitrate salts, which are important constituents of undesirable particulate matter, and also have an unpleasant odor. Thus, the amount of NH₃ injected must be carefully controlled and determine the optimum level of NH₃. A study from (Yun, 2012) indicated that the ratio of NH₃/NO_x equals on is the best to achieve highest purification rate of NO_x. Meanwhile, When the NH₃/NO_x=0.5, the maximum NO_x conversion remains at about 50% since the reducing agent NH₃ is not sufficient to convert the exhaust NO and NO₂ to N₂ via the standard reaction, and when the ration exceeds 1, the NO_x conversion decreases because of NH₃ inhibition and oxidation effect.

The table 2 descriptively shows the experimental and numerical conditions for catalyst temperature 224 °C. The outlet of exhaust gas temperature is 393.3 °C with space velocity 32570/h. The total engine-out NO_x is 118.6 ppm

and the ratio of NO₂/NO_x has been regulated to approach 0.5 as possible assisted by Diesel Oxidation Catalyst. The DOC catalyst plays an important role in reducing chemically the toxic gas CO to CO₂ and partially helping converting NO to NO₂.

For the experiment, the NH₃ injection and cut-off period are 200 seconds and 160 seconds respectively at engine speed 1600 rpm with NH₃/NO_x ratio equals 1.8. The amount of NH₃ injection should be optimized to avoid the NH₃ slip phenomenon, which is very undesirable as it is a waste of NH₃ and dangerous due to this flammable gas. The partial results have demonstrated a good agreement on outlet NO_x reduction between this experiment and simulation condition in both NH₃ supply and cut-off period as seen in figure 4. Therefore, this period has been taken for further analysis of SCR catalytic surface chemical species such as O₂⁻, H⁺, NH₄⁺, NH₄NO₃, NO₃⁻ and NO₂⁻ and as well as NO_x abatement performance to extensively investigate the way to improve the NO_x purification rate.

Table 2. Experimental and numerical conditions.

Engine speed rpm		1600 (25% load)
Exhaust gas temperature °C		393.3
Catalyst temperature °C		224
Space velocity 1/h		32570
Exhaust gas composition before SCR	NO _x ppm	118.6
	NO ₂ /NO _x	0.48
	O ₂ , H ₂ O, N ₂ ,	7.21, 8.43,
	CO ₂ %	75.7, 8.69
	φNH ₃	1.8
	supply period	200
NH ₃	sec	
	cut-off period	160
	sec	

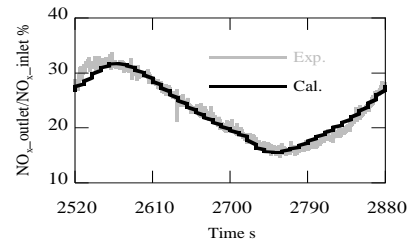


Figure 4. A well-matched between experimental and numerical results of outlet NO_x at 224°C.

The horizontal axis represents the time of calculation while the vertical axis represents the normalized concentration of studied surface chemical species on upstream/downstream and upper/lower layer of the catalyst

in figure 5. The numerical studies clearly demonstrated that it has very little variation between each single cell for each species. Therefore, in order to expediently and accurately analyze, 3 of 10 cells have been chosen. Cell number 2, 6 and 10 are selectively preferred for this surface chemical species adsorption/desorption investigation as seen in figure 5 (left).

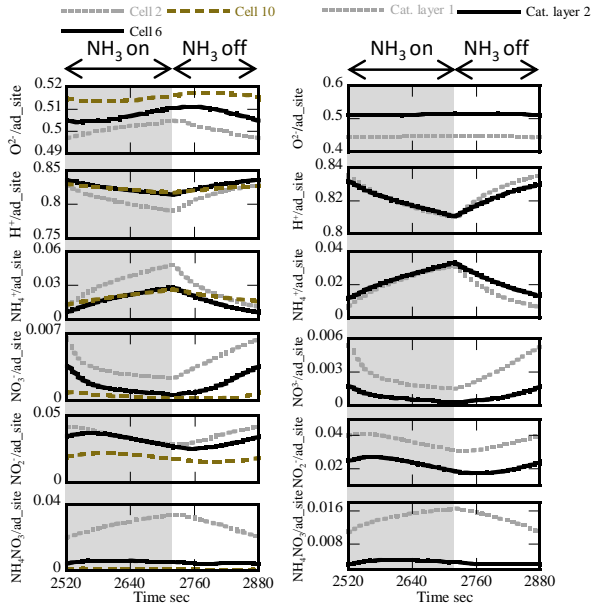


Figure 5. Analysis of surface chemical species at 224°C (left) on different cells, (right) on different catalyst layers.

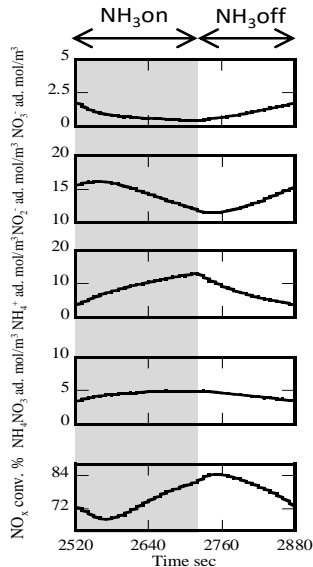


Figure 6. Analysis of NO_x conversion mechanism at 224°C.

The chemical species studied are O₂⁻, H⁺, NH₄⁺, NO₃⁻, NO₂⁻ and NH₄NO₃. There are slight variations of each

chemical species on different cells. The O₂⁻ and H⁺ involve a lot in the reactions on the earlier cells. Whereas, the concentrations of NH₄⁺, NO₃⁻, NO₂⁻ and NH₄NO₃ have a higher a value orderly on cell 2, 6 and 10. It appears that the chemical reactions occur actively on an earlier cells. Same things can be investigated on different catalyst layers as exposed in figure 5 (right). It can be defined that the reactions are more activated on layer 1 than that on layer 2 of catalyst.

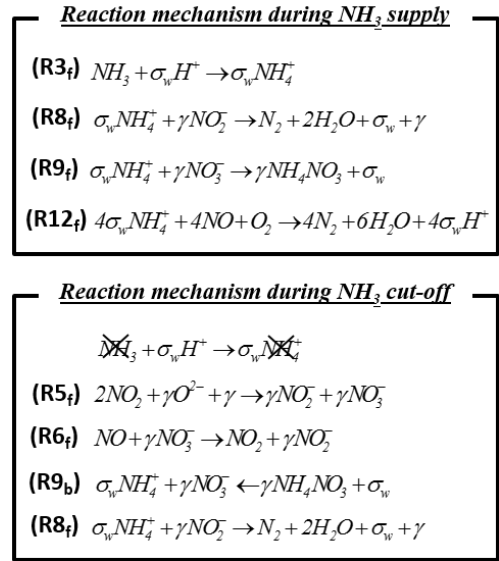


Figure 7. Chemical reaction mechanism during NH₃ supply and cut-off at 224 °C.

Furthermore, figure 6 and figure 7 demonstrate the analysis study on NO_x reduction process in both NH₃ supply and cut-off period. During the NH₃ supply, the NH₄⁺ is formed through forward reaction R3_f in figure 6 on the catalyst. Then, this formed NH₄⁺ reacts with NO₂⁻ and NO via reactions R8_f and R12_f resulting in increasing the outlet NO_x reduction rate. Simultaneously, the NH₄NO₃ is also formed via reaction R9_f in this period. After that, NH₃ injection is cut-off so that there is no NH₃ supply or NH₄⁺ added anymore for NO_x reduction. The concentrations of NO₃⁻ and NO₂⁻ are increased in this period due to reactions R5_f and R6_f. Remarkably; however, the NO_x conversion still stays at a high rate after immediately cutting-off NH₃ supply. As observed, the backward reaction R9_b occurs, which is the decomposition of NH₄NO₃, and generates NO₃⁻ and NH₄⁺. The R8_f also occurs resulted from the generated NH₄⁺ which helps maintain the NO_x conversion rate for a while.

3.2 Parametric study at catalyst temperature 280 °C

A parametric study has been performed at the catalyst temperature 280 °C for extensive investigation. This

simulation is performed by changing the temperature to 280 °C and space velocity while keeping other parameters the same as in conditions of 224 °C. The aim of this parametric study is to investigate the NO_x conversion efficiency at this temperature when the optimum of dt_{on} and φNH₃ at temperature 224 °C remain the same.

The analysis of adsorption/desorption of SCR surface chemical species on the different cells and on the first and second catalyst layer during the supply and cut-off NH₃ is to understand the diffusion between these cells and two layers of the catalyst. The numerical results confirm the very similar patterns of each species. The significance is that the concentration of reducing agent NH₄⁺ has involved more in reactions while the NH₄NO₃ is slower formed but faster decomposed in the NH₃ injection and cut-off period respectively. As a consequence, the total NO_x conversion at higher temperature achieves higher degree.

4. CONCLUSIONS

The study on analysis of SCR catalyst surface chemical species is a very crucial asset to understanding NO_x purification improvement. The SCR chemical reactions occur more active at the upstream and upper layer than that at downstream and lower layer of catalyst. Moreover, as suggested by the model, temporary supply and cut-off NH₃ shows the ability of enhancing total NO_x conversion attributed from NH₄NO₃ decomposition. The NO_x abatement rate is improved at appropriate higher catalyst temperature.

REFERENCES

- Colombo, M., Nova, I., Tronconi, E. & Schmeiber, V. (2011). NO/NO₂/N₂O-NH₃ SCR reactions over a commercial Fe-zeolite catalyst for diesel exhaust aftertreatment: Intrinsic kinetics and monoliteconverter modelling. *Applied of Catalyst B: Environmental* 111-112 (2012) 106-118.
- Grossale, A., Nova, I., Tronconi, E., Chatterjee, D., Weibel, M., (2008). The chemistry of NO/NO₂-NH₃ “fast” SCR reaction over Fe-ZSM5 investigated by transient reaction analysis. *Journal of Catalysis* 256 (2008) 312-322.
- Koebel, M., Elsener, M., Kleemann, M., Urea-SCR (2000). A promising technique to reduce NO_x emissions from automotive diesel engines. *Catalysis Today* 59 (2000) 335-345.
- Kröcher, O., Devadas, M., Elsener, M., Wokaun, A., Söger, N., Pfeifer, M., Demel, Y., & Musmann, L. (2006). Investigation of the selective catalytic reduction of NO by NH₃ over Fe-ZSM5 monolith catalysts. *Applied Catalysis B: Environmental*, 66, 208-216.

Yun, B. K. & Kim M. Y. (2012). Modeling the selective catalytic reduction of NO_x by ammonia over a Vanadia-based catalyst from heavy duty diesel exhaust gases. *Applied Thermal Engineering*: 50 (2013) 152-158.

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